

# OPTICAL PROPERTIES AND CORROSION RESISTANCE OF DURABLE SILVER COATINGS

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## ABSTRACT

There is a need in the optics community for highly reflective mirrors that do not degrade in harsh environments. While silver can be a highly efficient reflector of visible light, it suffers from poor resistance to corrosive atmospheric gases. Here, we investigate a durable silver coating scheme, in which silver is sputter deposited between very thin layers of nichrome nitride. Excellent corrosion resistance is achieved with a silicon nitride overcoat. Samples were exposed to a variety of atmospheres and it was found that the nichrome nitride dramatically increased corrosion resistance when compared to bare silver or silicon nitride coated silver. Similar results were found when electrochemical impedance spectroscopy was used to evaluate samples. The enhanced corrosion resistance is achieved even when the thickness of the nichrome nitride adhesion layer is too thin to be considered continuous.

## INTRODUCTION

Front surface mirrors are commonly used as broad-band reflectors in many optical systems. Bare silver possesses better reflectivity of visible light than many other metals including aluminum. Higher reflectivity means that less light energy is wasted by being converted to heat. However, bare silver is quite reactive and its optical properties are easily degraded by a number of common atmospheric compounds including salt fog, ozone, acids, chlorine and sulfur compounds.[1] It would be quite advantageous to deposit a material that will provide protection without degrading silver's desirable optical properties.

One scheme has been proposed and demonstrated by Wolfe et al.[2,3] It involves a very thin interlayer of NiCrNx between the substrate and the silver film and another interlayer between the silver film and a 100Å layer of silicon nitride. The interlayer between the SiNx and the Ag can average 10Å or less. In fact, Wolfe presented a TEM micrograph that showed that the interlayer formed noncontinuous islands when deposited in their in-line magnetron sputter coater. They reported that the presence of the NiCrNx layer was essential to providing good chemical durability. The fact that such a thin, noncontinuous layer can provide protection is intriguing. We will attempt here to reproduce the corrosion resistant configuration and study the mechanism by which the coating provides durability.

Electrochemical techniques have been developed to rapidly assess the corrosion resistant quality of coatings for a variety of industries. Electrochemical Impedance Spectroscopy (EIS) is one technique which involves exposing a coated sample to an electrolytic solution like sodium chloride. The impedance of the sample, protective layer, and electrolytic solution are all measured as a function of frequency. By analyzing the frequency response, one can evaluate the material. In many cases, impedance spectra permit an early observation of film deterioration, long before visually observable changes occur. Furthermore, even though it is a solution based technique, EIS data has been correlated to atmospheric exposure like continuous salt fog testing.[4] EIS has also been used to study metal coatings experiencing a loss of adhesion.[5] While this technique has been well developed, to our knowledge, this is the first

time it has been used to evaluate optical materials. It may show promise as a rapid, quantitative alternative to the salt fog and humidity testing used to qualify field optics.

## EXPERIMENT

All films were deposited in a cryopumped chamber equipped with 4 rf sputter guns employing 2 inch targets. The substrates were loaded on to a carousel that rotated at 40 rpm. 22 sccm of Ar and 4.4 sccm of N<sub>2</sub> flowed into the chamber and the pump was throttled to achieve a pressure of 0.53Pa (4.0 mT). Specific deposition parameters are given in the table below. The substrates used were test quality silicon wafers and fused silica. Thickness values for silver and silicon nitride were obtained from QCM deposition rate monitors that were calibrated to much longer depositions via optical and profilometer techniques. The thickness values for NiCrNx were based on deposition time calibrated to thicker films.

Table I. Deposition conditions

Compound	Thickness	Rate	Target	rf Power
NiCrNx	8 Å	0.02-0.2 Å/s	80Ni 20Cr	20-100 W
Silver	1200 Å	1.00 Å/s	Silver	100 W
NiCrNx	2-8 Å	0.02-0.2 Å/s	80Ni 20Cr	20-100 W
SiNx	100 Å	0.16 Å/s	Silicon	200 W

Some films were exposed to acid vapor to accelerate degradation. These samples were suspended in a closed container for 24 hours over a solution of 1ml conc. HCl, 1 ml conc. H<sub>2</sub>SO<sub>4</sub> and 218ml of deionized water to give about pH 1. The solution was allowed to come to thermal equilibrium after mixing to prevent condensation onto the suspended samples. Electrochemical Impedance Spectroscopy (EIS) was performed on other samples in 0.1N NaCl in a Gamry Instruments Paint Test Cell. Data was collected with a Gamry Instruments CMS300 EIS System, which scans from high to low frequency. Specular reflection spectra were collected on a Perkin Elmer Lambda 9 Absorption Spectrometer as well as a SCI FilmTek 2000 Fiber Optic Reflectometer.

## RESULTS

The reflection spectra of several samples are given in figure 1. Bare silver has a reflectivity of near 98% at longer wavelengths, decreasing dramatically below 400 nanometers. When 100Å of SiNx is deposited on top of the silver film, the reflectivity is enhanced slightly above 380nm at the expense of reflectivity below 380nm. The addition of 2Å of NiCrNx followed by SiNx causes a drop in reflectivity between 1% and 9%. To compensate for the absorption loss, a two layer dielectric layer (504 nm silica and 480 nm of titania) was added to enhance the short wavelength reflection at the expense of the long wavelength reflection. Samples with the reflectivity enhancement layers are notated by peAg. Notice that the films with the thicker NiCrNx interlayers show further reduced reflectivity.

Several samples were exposed to acid vapor for 24 hours. Figure 2 shows the reflection spectrum of each sample before and after exposure. The silver film showed severe degradation. The film corroded uniformly and the reaction product seems to absorb light below 550 nm. The silicon nitride coated silver film also severely degrades, but much of the reduction in specular reflection is due to scattered light. Under an optical microscope, these films looked as if corrosion products had grown from point defects and grown into large “colonies”. Total Integrated Scatter measurements at 632.8nm showed that 21% of the loss in specular reflection

is due to increased scatter as might be associated with delamination and increased texture. The SiN<sub>x</sub>/NiCrN<sub>x</sub>/Ag film survived the acid exposure well. Only a small loss in reflectivity was evident and under the microscope few defects were observed. It should be noted that these spectra are measured relative to a standard. Reflectivities above 100% are valid relative to other samples.

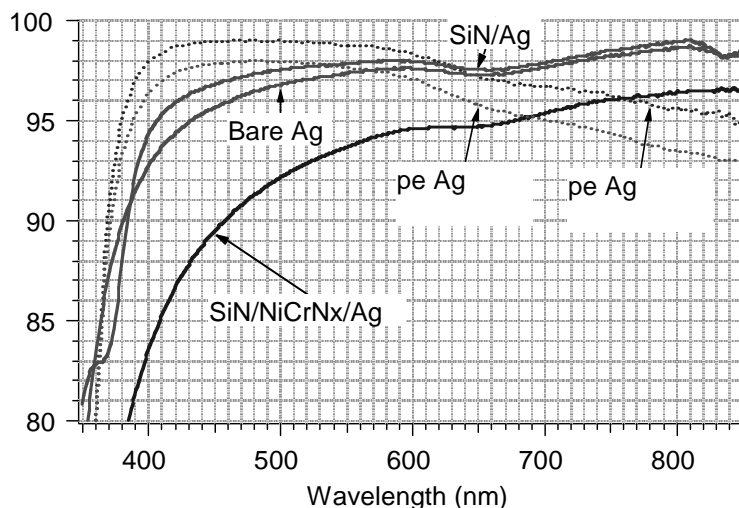


Figure 1. Reflection spectrum of Silver films with various coatings. The incident angle was 6° from normal.

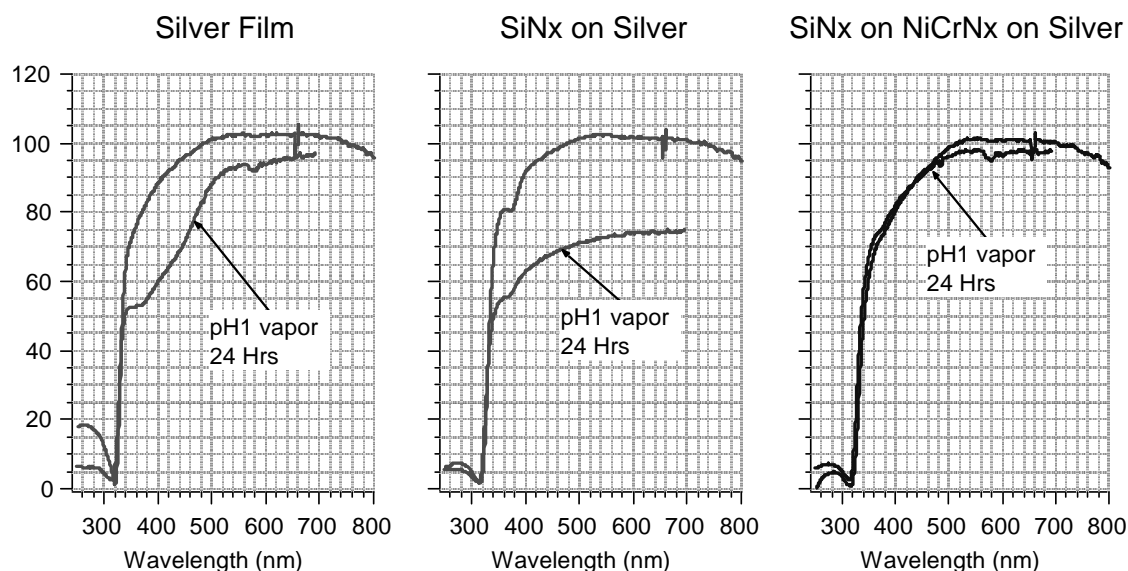


Figure 2. Reflection spectrum of Silver films with various coatings before and after exposure to acidic vapor. The incident angle was 6° from normal.

### **Electrochemical Impedance Spectroscopy**

In order to characterize the protective films more fully, three samples were exposed to a 0.1N NaCl solution followed by an impedance scan. The equivalent circuit model shown in figure 4 was chosen to represent the physical system.[6]  $R_s$  represents the solution resistance,  $R_f$  represents the coating resistance,  $C_f$  represents the coating capacitance,  $C_d$  represents the

double layer capacitance, and  $W$  represents a Warburg impedance, which models a case when charge transfer is diffusion controlled.[7] The Warburg element will be fit with a parameter  $\sigma$  which has units of  $\text{Ohms}/\text{Hertz}^{1/2}$ .

Figure 5a shows the impedance spectrum of a bare silver film. Since impedance is a complex quantity, it can be defined in terms of an absolute magnitude and a phase. A pure resistor has a phase of zero and a pure capacitor has a phase of -90 degrees. The crosses are data points. The solid line is an experimental fit based on the model above. The fit parameters are  $R_s=10.5\Omega$ ,  $C_d=300\mu\text{F}$ , and  $\sigma=3000\Omega/\text{Hz}^{1/2}$ .  $R_f$  and  $C_f$  are defined as zero since there is no protective layer on bare silver.

Figure 5b shows the impedance spectrum of silver with 100Å of silicon nitride deposited on top. The solid line is an experimental fit given the following parameters.  $R=13\Omega$ ,  $C_d=460\mu\text{F}$ ,  $\sigma=25000\Omega/\text{Hz}^{1/2}$ ,  $R_f=250\Omega$ , and  $C_f=600\mu\text{F}$ .

Figure 5c shows the impedance spectrum of silver with 2Å of NiCrNx followed by 100Å of silicon nitride deposited on top. The solid line is an experimental fit given the following parameters.  $R_s=13\Omega$ ,  $R_f=10^9\Omega$ , and  $C_f=700\mu\text{F}$ . The fit was insensitive to  $C_d$  and  $\sigma$  at any reasonable values, so they were set to zero.

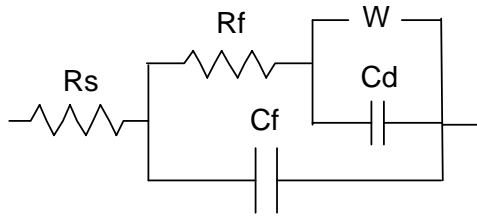


Figure 4. Equivalent Circuit Model for a coated metal in solution.

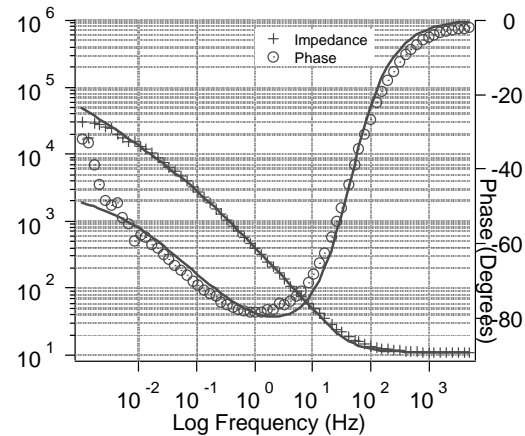


Figure 5a. EIS of bare Ag

The most important parameter here is  $R_f$ . When one compares the values with and without the NiCrNx interlayer ( $10^9\Omega$  versus  $250\Omega$ ), it is obvious that the interlayer has a dramatic effect on the ability of ions to pass through the silicon nitride. The reasons for this will be discussed in the next section. In addition, it must also be noted that the fit at the lowest frequencies was poor. Data collection is quite slow at low frequencies and the signal is weak. It is also quite possible that the surface is changing during the course of the scan. While more complicated circuit models might fit the data more accurately, this model is attractive in that it fits each of three different cases and each element has a physical meaning.

## DISCUSSION

The vapor exposure and EIS data correlate quite well. In order for the vapor to react with the silver film, it must pass through the silicon nitride layer. In order to measure conductance through the silicon nitride layer, ions must be able to pass through the film. Both experiments lead to the conclusion that the SiNx film is much less permeable in the presence of the NiCrNx interlayer. EIS is much more quantitative, suggesting that in the presence of the interlayer, the silicon nitride film is less permeable by over 6 orders of magnitude. The mechanism behind the additional protection is not clear, but let's assume that there are two possible explanations. The

first is that the NiCrNx simply provides an adhesion layer between the silver and the silicon nitride. In this case, one could assume that the number of pinholes and other defects in the silicon nitride is the same regardless of whether the NiCrNx is present. Wolfe speculated that the NiCrNx layer is really an admixture of Ni and CrNx. Perhaps the nickel adheres well to the silver and the chrome nitride adheres well to the silicon nitride. When the silver is attacked through one of the defects in the silicon nitride film, the reactant might rapidly react at the silicon nitride/ silver interface, delaminating the silicon nitride film exposing more silver surface to the corrosive solution. In this scenario, the presence of the NiCrNx layer would serve to prevent that delamination, which would minimize the growth rate of the area of silver exposed to the corrosive environment.

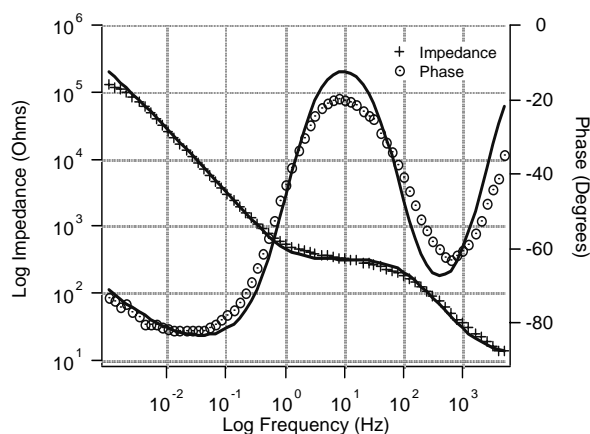


Figure 5b. EIS of SiNx on Ag

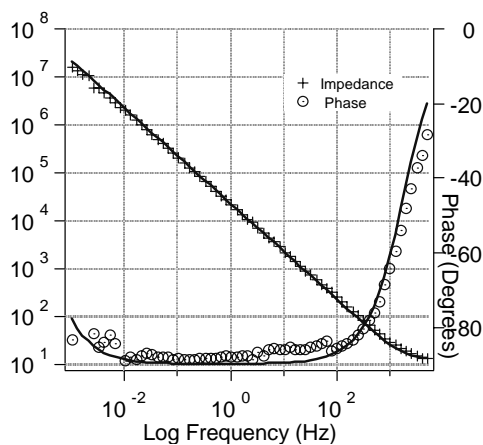


Figure 5c. EIS of SiNx on 2Å NiCrNx on Ag

Another possible explanation is that the NiCrNx changes the surface of the silver in such a way that changes the morphology of the silicon nitride film. In this case, the additional protection is achieved by growing a film that simply has less defect density, minimizing the area exposed to the corrosive atmosphere or electrolytic solution. Perhaps the NiCrNx provides more nucleation sites for SiNx film growth relative to bare silver. In the presence of many nucleation sites, subsequent depositing adatoms need not diffuse far before finding a low energy site on the growing film. If this is true, complete coverage might be obtained very rapidly, decreasing shadow effects that might accentuate void formation. In this way tiny defects may be avoided. Of course, once a complete silicon nitride coverage is achieved, the growth of the film should not depend on the presence of an interlayer, but certainly, the morphology of grains and voids are dependent on the nucleation conditions.

Several other facts are germane to this discussion. Wolfe and we found that deep scratches in a protected film did not change its corrosion behavior in reactive atmospheres. In addition, TEM micrographs showed features in Wolfe's samples consistent with island formation of NiCrNx. In this work, TEM of slightly thicker films (8Å) showed features that were consistent with continuous layers. Samples with 2Å interlayers were too thin to image. Lastly, optical micrographs of samples taken after EIS, show that without an interlayer, there was a high density of defects of various sizes; many had coalesced. Samples with the interlayer showed a very low defect density, but those defects were quite large.

The fact that continuous and noncontinuous NiCrNx both perform well is evidence that the interlayer protects by improving the quality of the film. The great difference in  $R_f$  generated by modelling the impedance spectrum also supports the idea that the interlayer either decreases defect density or fantastically decreases the defect size. If one assumes that the change in  $R_f$  is

due to a change in defect area and if one assumes that the silicon nitride defects are of a uniform size, and that the defect density is the same in both cases, a 4,000,000 times increase in defect area would require a factor of 2000 increase in defect radius. (as predicted by EIS) If a small defect was 10 nm, a large defect would have to be 20 microns, no such large defects were visible, nor are they likely to be formed by rf sputtering.

## CONCLUSIONS

The silver protection scheme proposed by Wolfe et al. has been reproduced in a different deposition geometry under different deposition conditions. No evidence of NiCrNx islands were found. Corrosion testing in acidic vapor correlated well with the EIS data and it was shown that the NiCrNx interlayer is crucial to affording protection. All of the data support the hypothesis that the NiCrNx serves as a seed layer for growing high quality silicon nitride films.

## ACKNOWLEDGMENT

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## REFERENCES

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- 1 D.W. Rice et al., *J. Electrochem. Soc.* **128**(2) p. 275-284 (1981)
- 2 J.D. Wolfe, R.E. Laird, C.K. Carniglia, J.P. Lehan, *Technical Digest OSA 1995 Optical Interference Coatings Conference* p. 115-117
- 3 N. Thomas et al., *Technical Digest OSA 1998 Optical Interference Coatings Conference*
- 4 P. Kamarchik, in *Electrochemical Impedance: Analysis and Interpretation*, edited by J.R.Scully, D.C. Silverman, and M.W. Kendig (Am. Soc. Test. Mater. STP **1188**, Philadelphia, 1993, ), p. 463-474.
- 5 M.W. Kendig, S. Jeanjaquet, and J.Lumsden, in *Electrochemical Impedance: Analysis and Interpretation*, edited by J.R.Scully, D.C. Silverman, and M.W. Kendig (Am. Soc. Test. Mater. STP **1188**, Philadelphia, 1993, ), p. 407-427.
- 6 M.W. Kendig, S. Jeanjaquet, R. Brown, and F. Thomas, *J. Coatings Tech.* **68**(863) p 39-47
- 7 D.C. Silverman, in *Electrochemical Techniques for Corrosion Engineering*, edited by R. Baboian (National Association of Corrosion Engineers, Houston TX, 1985) p. 73-79

### **Reference Data**

P.D. Fuqua and J.D. Barrie, "Optical Properties and Corrosion Resistance of Durable Silver Coatings", In *Properties and Processing of Vapor-Deposited Coatings*, edited by R. Johnson, W. Lee, M. Pickering, B. Sheldon (Mater. Res. Soc. Proc. **555** Pittsburgh, PA, 1998) pp. 85-90

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